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Degradation of tannic acid powered by TiO_2 nanoparticles

N. Lakshmi Kruthika, G.Bhaskar Raju* S.Prabhakar
National Metallurgical Laboratory Madras Centre
CSIR Madras Complex, Taramani, Chennai-600113, India
Email: gbraju55@gmail.com, Fax: +91-44-22542077

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Abstract: The wastewater from the coir, pharmaceutical, leather, paper and pulp industries is contaminated with water-soluble poly phenolic compounds (tannins). Among various tannins, tannic acid is a typical hydrolysable tannin prevalent in wastewater. The degradation of tannic acid using TiO_2 nanoparticles as photocatalyst was investigated. The effect of catalyst concentration, pH of aqueous suspension and also electron acceptors such as hydrogen peroxide (H_2O_2) and ozone (O_3) on the degradation of tannic acid was studied. The degradation of tannic acid was found to be more efficient and complete in the presence of $UV/TiO_2/O_3$ compared to $UV/TiO_2/H_2O_2$. The kinetics of degradation was observed to follow first order rate equation which indicates that the mineralization process is diffusion controlled.

1. Introduction:

In 1972, light induced water splitting on TiO_2 surface was reported by Fujishima and Honda which lead to novel approach in heterogeneous catalysis [1]. The TiO_2 is an excellent photocatalyst [2-4] because of its high stability, affordability and capability to mineralize variety of organic compounds [5-7]. Photons with energy higher than the band gap energy (Eg) of the semiconductor excite electrons from the valence band to the conduction band and form charge pairs consisting of a hole (h^+) and electron (e^-) [8]. These charge carriers either recombine inside the particle or migrate to its surface, where they can react with adsorbed molecules. In aqueous solutions, positively charged valence-band holes typically form hydroxyl radicals (·OH) at the surface of TiO_2, while electrons in the conduction band mainly reduce dissolved molecular oxygen to super oxide $\cdot O_2^-$ radical anions. The organic molecules present in the solution may react with these oxidizing agents inducing their oxidative degradation to carbon dioxide and water [9]. It was demonstrated that the technology has potential to reduce water contaminants and eliminate the use of toxic catalysts [10]. The photo catalytic performance of TiO_2 depends not only on its bulk energy band structure but also, to a large extent, on its surface properties. The photocatalytic activity was found to increase by increasing the surface area [11]. The TiO_2 nanomaterials are successfully used for the photocatalytic remediation of a variety of organic pollutants such as CCl_4, $CHCl_3$, phenols, chlorinated phenols, pyridine, pesticides, and organic dyes as well as reductive deposition of heavy metals such as Pt^{4+}, Pd^{2+}, Au^{3+}, Rh^{3+} and Cr^{3+} from aqueous solutions[12-15]. The TiO_2 nanomaterials were found to be efficient for the destruction of biological materials such as bacteria, viruses and molds [16].

One of the disadvantages of this catalyst is that its activity is still not high enough for commercial application [17]. Advanced oxidation technologies (AOTs), which involve the *in situ* generation of highly potent chemical oxidants such as ·OH, have emerged as an important class of technologies for accelerating the oxidation (and hence the removal) of a wide range of organic contaminants in

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water. Hence combination of photocatalysis and ozonolysis was attempted for the degradation of tannic acid. Tannins are water-soluble poly phenolic compounds having a molecular weight between 500 and 3000. The wastewater from the coir, pharmaceutical, leather, paper and pulp industries is contaminated with tannins [18, 19]. Among various tannins, tannic acid is a typical hydrolysable tannin prevalent in wastewater [20]. Tannic acid has a large number of phenolic hydroxyl groups (anionic) with a molecular weight of 1701 ($C_{76}H_{52}O_{48}$) and a solubility of 300 g/L in water. Due to its natural origin and wide distribution, tannic acid has been widely used as a surrogate or model compound of Dissolved Organic Matter (DOM) in environmental studies [21]. It is toxic to aquatic organisms such as algae, phytoplankton, fish and invertebrates. So tannic acids are known refractory organic pollutants in water [22,23]. Tannic acid may also interact with toxicants in aquatic ecosystems and change their toxicity [21]. The conventional processes used for the removal of tannic acid from wastewater include biological treatment [24-26], ultrafiltration and adsorption.

In this paper, the photocatalytic degradation kinetics of tannic acid in aqueous TiO_2 suspensions was presented. The effects of concentration of photocatalyst, initial concentration of tannic acid, pH of aqueous suspension, concentration of H_2O_2 and O_3 on the photocatalytic degradation of tannic acid were discussed.

2. Experimental Materials and Methods

2.1. Materials: All the chemicals used in the experiments were of analytical grade. Double distilled water free from carbon was employed. The photocatalyst, TiO_2 used for the degradation of tannic acid was obtained from SRL chemicals. The size of the TiO_2 nanoparticle is 7 nm. The pH of the aqueous solutions was adjusted using dilute H_2SO_4 or NaOH solutions.

2.2. Photoreactor and light source: The radiation source (HML-LP 88) was a high pressure mercury vapor lamp which emits a monochromatic light at 365 nm. The sample holder is made of silica glass reactor with an inlet and outlet for ozone gas. Arrangements were made so that the test solution is circulated through a thermostat to maintain the temperature at 25°C.

2.3 Ozone generator: The corona discharge ozone generator (Model: L10G) supplied by Faraday Instruments, Coimbatore, India was used to generate ozone. Oxidation of tannic acid in the presence of UV/O_3 and $UV/TiO_2/O_3$ was carried out. Ozone was passed through the sample solution of tannic acid at a constant flow rate.

2.4. Procedure and analysis: The tannic acid solution at natural pH (≈ pH 6) was magnetically stirred in the presence of TiO_2 for 1 h to reach the adsorption equilibrium before UV irradiation. Samples of 2 ml were collected at regular intervals and analyzed by TOC analyzer (Shimadzu VCSN/CPN Model). The homogenized diluted sample was injected in to reaction chamber packed with catalyst. The carbon is oxidized to CO_2 in the reaction chamber and the CO_2 gas generated is quantitatively estimated by non-dispersive infrared analyzer. The TOC was deduced from the measurements of total carbon and inorganic carbon.

3. Results and Discussion

3.1: Characterization of TiO_2 nanoparticles:

The X-ray difractogram of TiO_2 nano particles is shown in Fig 1. The 2θ values at 25.4, 27.3, 36.96, 48.32 and 55.16 clearly indicates that the TiO_2 is in anatase phase. The strong peak at the 2θ value of 25.4 can be indexed to the (101) phase of anatase. The scanning electron micrograph of TiO_2 powder shown in Fig 1b indicates spherical morphology. The tendency of agglomeration of nano particles is also evident due to high surface energy of the particles.

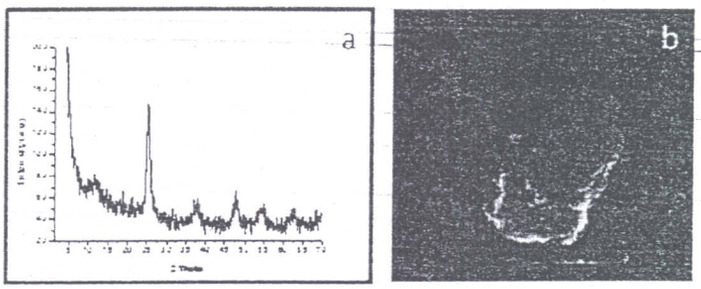

Fig. 1. a) The X-ray difractogram of TiO_2 nanoparticles b) scanning electron micrograph of TiO_2 nanoparticles

The surface area and pore size of TiO_2 powder was estimated using BET analyzer. The BET and Langmuir surface areas were observed to be 632.93 m^2/g and 1767 m^2/g respectively. The total pore volume of pores was found to be 1.084 cm^3/g and the average pore diameter is 61.2 Å.

3.2: Tannic acid degradation by various processes

The removal of Tannic acid was studied under seven different experimental conditions: (i) under UV irradiation (photolysis), (ii) in the presence of TiO_2 alone, (iii) O_3 (ozonolysis) (iv) UV/O_3, (v) UV/TiO_2 (photocatalysis), (vi) $UV/TiO_2/H_2O_2$ and (vii) $UV/TiO_2/H_2O_2/O_3$. The decrease in the concentration of tannic acid is plotted as a function of time (Fig 2). In the presence of TiO_2 and without irradiation, it was observed that around 25 ppm of tannic acid was decreased. This decrease was attributed to adsorption of tannic acid molecules onto the surface of TiO_2 particles.

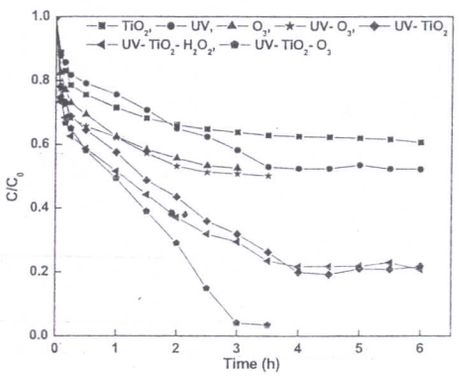

Fig. 2. Degradation of tannic acid under different experimental conditions (Initial concentration of tannic acid: 100 mg L^{-1}, TiO_2: 10 mg L^{-1}, H_2O_2: 0.0077M, UV: 365nm, O_3: 0.5g/h)

The adsorption of tannic acid on TiO_2 was substantiated by FT-IR studies. The FT IR spectrum of tannic acid is presented in Fig 3. The broad band in the region of 3300-3500 cm^{-1} is the characteristic of inter molecular hydrogen bonded -OH groups of tannic acid. Strong and intense band at 1721 cm^{-1} is attributed to the stretching vibration of carbonyl group, characteristic of organic acids [27]. The bands at 1447 and 1368 cm^{-1} are attributed to aliphatic C-H stretching and bending vibrations of CH_2 groups of tannic acid [28]. The FT IR spectrum of TiO_2 is presented in Fig 3b. The broad band around 3412 cm^{-1} was attributed to the superposition of the hydroxyl groups involved in hydrogen bonding and symmetric and asymmetric modes of molecular water co-ordinated to Ti^{4+} cations [29]. The broad band at 750 cm^{-1} is assigned to TiO_2 lattice vibrations. The FTIR spectrum of the tannic acid equilibrated with TiO_2 particles (Fig 3c) exhibited the bands related to tannic acid and TiO_2 powder. Thus the adsorption of tannic acid on TiO_2 particles is evident.

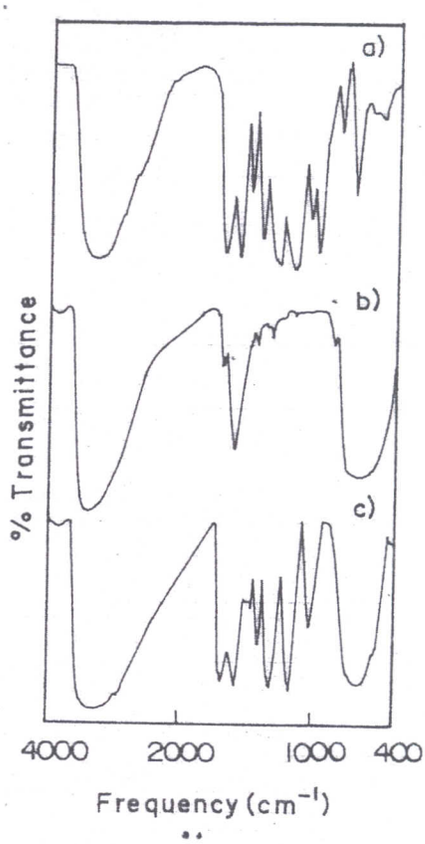

Fig 3. FT IR Spectra of a) tannic acid b) TiO_2 nano particles and c) TiO_2 powder after equilibration with tannic acid.

From Fig 2, it is also apparent that the effect of UV irradiation and ozonation on the degradation of tannic acid is marginal in the absence of TiO_2. However, in the presence of TiO_2, the degradation of tannic acid was found to be effective. Around 84 % of tannic acid was degraded within 5 h. When H_2O_2, an electron acceptor was injected in to the reaction mixture, slight improvement in

degradation was observed. But when O_3 was passed through the TiO_2 suspension under irradiated condition, almost complete removal (98%) was observed in 3 h. The enhanced degradation under $UV/O_3/TiO_2$ may be attributed to the in situ generation of hydroxyl radical.

3.3. Effect of TiO_2concentration:

The concentration of photo catalyst dosage on the degradation of tannic acid in aqueous solution was studied both in the presence and absence of H_2O_2. The results are presented in Fig 4. The degradation was improved by increasing the amount of TiO_2 from 5 mg L^{-1} to 10 mg L^{-1}. Thereafter, the improvement in degradation is very marginal. The increased mineralization could be explained due to increased surface area of TiO_2 and the number of active sites available for the photo catalytic reaction. However, when TiO_2 is overdosed, the number of active sites on the TiO_2 surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area caused by agglomeration (particle-particle interactions) at high solid concentration [30-31]. Therefore, 10 mg L^{-1} of TiO_2 was selected as the optimal amount of photo catalyst in subsequent experiments.

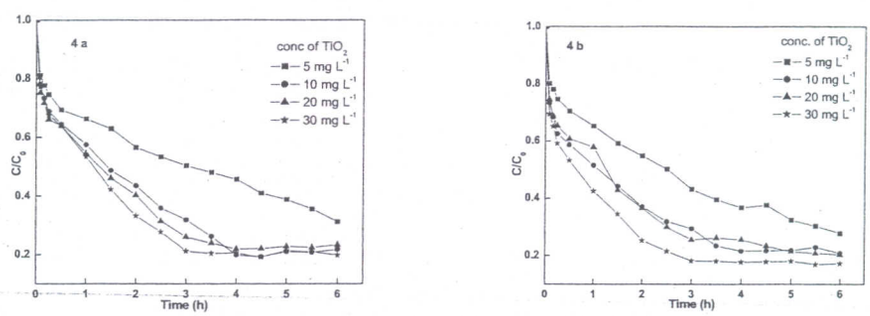

Fig. 4. Effect of TiO_2 concentration on tannic acid removal (a) in the absence of H_2O_2 (b) in presence of H_2O_2 (Initial concentration of tannic acid: 100 mg L^{-1}, H_2O_2: 0.0077 M, UV: 365 nm)

3.4: Effect of tannic acid concentration:

The effect of initial concentration of tannic acid in the range of 50 mg L^{-1} to 200 mg L^{-1} on the photocatalytic degradation and the kinetics of degradation was investigated and the experimental results are presented in Fig 5 in Fig 6. It is evident from the graph that at lower concentrations of tannic acid, the reaction follows the first order kinetics but at higher concentrations, it transforms to zero order kinetics.

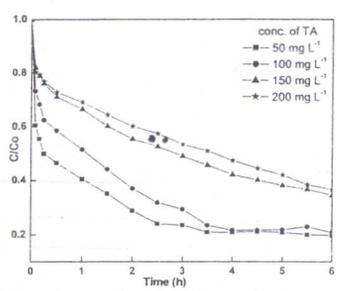

Fig. 5. Effect of initial tannic acid concentration on degradation rate (TiO_2:10 mg L^{-1}, H_2O_2: 0.0077 M, UV: 365 nm)

This can be explained from the following rate equation [1].

$$\text{rate} = \frac{-dc}{dt} = \frac{\varepsilon P k_c[C] / V}{k_c[C] + \Sigma_i k_{Si} [S_i]} \quad (1)$$

where ε is a constant [mol s^{-1} kW^{-1}] that depends on system and technology, P is electric power input [kW], V is treated volume [L], C is TOC or concentration of the organic contaminant, k_c is rate constant and S is scavenger. Since the goodness of fit (R^2) for zero order rate equation is poor, the graphs pertaining to zero order rate equation were not presented. First order kinetics indicates that the process is diffusion controlled and rate- limiting arrival of the tannic acid at the surface of TiO_2 [32].

If [C] is high so that $kc\,[C] >> \Sigma_i k_{Si}\,[S_i]$, then the reaction rate will be zero order.

If [C] is low so that $kc\,[C] << \Sigma_i k_{Si}\,[S_i]$, then the reaction rate will be first order.

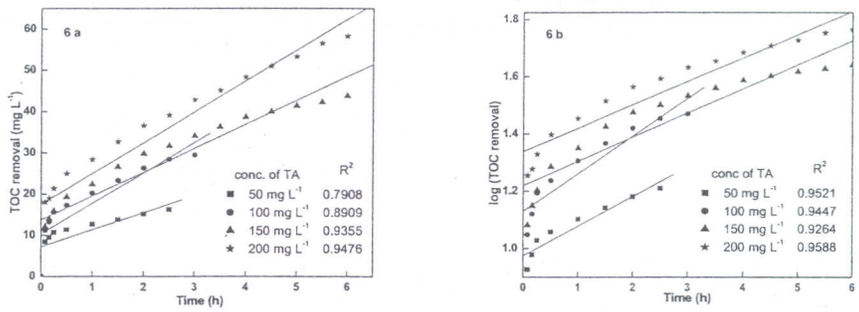

Fig. 6. (a) Zero order and (b) First order kinetics graphs of Tannic acid removal at various substrate concentrations (other conditions same as Fig 5).

3.5. Effect of pH:

The pH of the solution dictates the surface charge of the photocatalyst and size of aggregates it forms [30]. Therefore, the degradation of the pollutant was studied at three different pH values (pH 3, 6 & 10). The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of H_2SO_4 or NaOH.

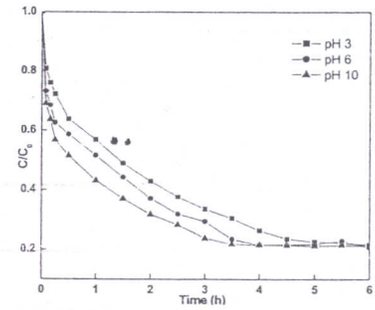

Fig. 7. Effect of pH on the photocatalytic degradation of tannic acid (Initial concentration of tannic acid: 100 mg L^{-1}, TiO_2: 10 mg L^{-1}, H_2O_2: 0.0077 M, UV: 365 nm)

The depletion of the tannic acid is shown in Fig 7. It was found that the rate increases with the increase in reaction pH and maximum effect was observed at pH 10. Better degradation in alkaline pH could be attributed to efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of hydroxide ion.

3.6. Effect of H_2O_2 concentration: In order to study the effect of electron acceptor H_2O_2, the degradation process was carried out at various H_2O_2 concentrations and the depletion is reported in Fig 8. It is apparent that the effect of hydrogen peroxide concentration on TOC depletion is negligible which is also evident from the zero order kinetics of the reaction.

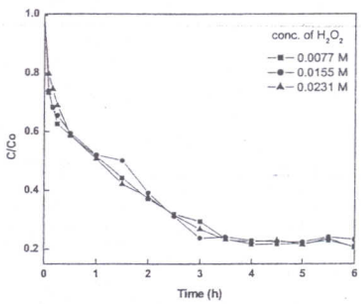

Fig. 8. Effect of H_2O_2 concentration on the removal of tannic acid (Initial concentration of tannic acid: 100 mg L^{-1}, TiO_2: 10 mg L^{-1})

3.7. Effect of O_3 concentration:

In order to understand the influence of ozone flow on the reaction rate, the reaction was carried out at various ozone flow rate viz 0.5, 1.0, 1.5 and 2.0 g/h. From the results shown in Fig. 9, it is evident that the degradation was improved to 97 % by increasing the ozone flow rate. The increase in the mineralization of tannic acid with O_3 flow rate supports the first order kinetics i.e, the process is diffusion controlled [33]. Therefore, it can be concluded that tannic acid degradation by photocatalysis in presence of O_3 proceeds by the oxidation of tannic acid by hydroxyl radical.

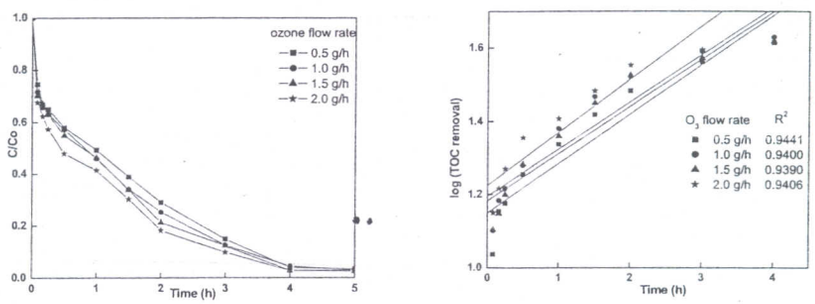

Fig. 9. Effect of ozone flowrate on tannic acid depletion (Initial concentration of tannic acid: 100 mg L^{-1}, TiO_2: 10 mg L^{-1}, UV: 365 nm)

The decomposition of ozone in the presence of UV radiation is well established by earlier researchers. The generation of oxygen and hydrogen peroxide from ozone can be represented by the following equations.

$$O_3 + h\upsilon \rightarrow O_2 + [O] \quad (2)$$

$$O_3 + H_2O + h\upsilon \rightarrow H_2O_2 + O_2 \quad (3)$$

Also, the hydroxyl radicals are generated by self-decomposition of H_2O_2 in the presence of UV light and reaction between H_2O_2 and O_3.

$$H_2O_2 + h\upsilon \rightarrow 2OH^{\cdot} \quad (4)$$

$$O_3 + H_2O_2 \rightarrow 2OH^{\cdot} + 3O_2 \quad (5)$$

$$[O] + H_2O \rightarrow 2OH^{\cdot} \quad (6)$$

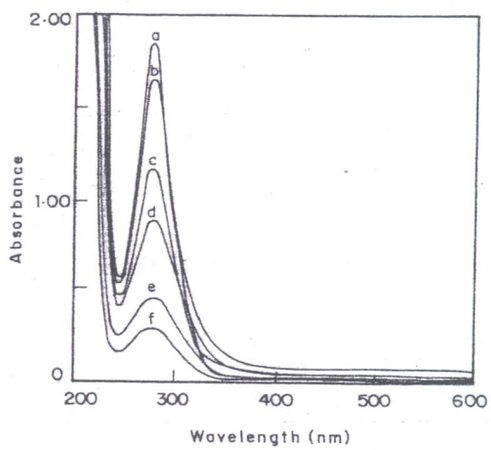

Fig. 10. UV-Visible spectrum of tannic acid with time. a) Initial, b) after 1 h, c) after 2 h, d) after 3 h, e) after 4 h, f) after 5 h. (Reaction conditions Initial concentration of tannic acid 100 mg L^{-1}, TiO_2: 10 mg L^{-1}, UV: 365 nm, O_3: 0.5 g/h)

These hydroxyl radicals oxidize tannic acid directly to CO_2. This can be proved from the UV-Visible spectra of the reaction samples taken at regular intervals. The UV-Vis spectrum shows characteristic tannic acid peak at 274 nm. As reaction proceeds, the intensity of the peak decreased but no other peak was noticed (Fig 10). The decrease in TOC and the intensity of UV Peak with time clearly indicates that the tannic acid is mineralized during advanced oxidation process.

4. Conclusion

The results of this study clearly suggests that the TiO_2 can be used as photocatalyst for the decomposition of tannic acid in the presence of UV-light and Hydrogen peroxide/ ozone. Ozone was found to be more efficient than hydrogen peroxide. The photocatalytic degradation of tannic acid in aqueous TiO_2 suspensions follows a pseudo-first-order kinetics. The increase in ozone flow rate markedly enhances the degradation rate of the pollutant.

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